

## SOIL PROPERTIES OF A MARKOWICE RACIBÓRZ DISTRICT AFTER THE FLOOD

EWACEBULA<sup>1</sup>, JAN CEBULA<sup>2</sup>, JERZY CIBA<sup>1</sup>, BRONISŁAW WYŻGOLIK<sup>3</sup>

<sup>1</sup> Silesian University of Technology, Faculty of Chemistry  
ul. Krzywoustego 6, 44-100 Gliwice, Poland

<sup>2</sup> Silesian University of Technology, Faculty of Energy and Environmental Engineering  
ul. Konarskiego 18, 44-101 Gliwice, Poland

<sup>3</sup>Institute of Environmental Engineering of the Polish Academy of Science  
ul. M. Skłodowskiej-Curie 34, 41-819 Zabrze, Poland

Keywords: soils, heavy metals, pollution, flood.

### WŁAŚCIWOŚCI GLEB RACIBORZA-MARKOWIC PO POWODZI

W pracy przedstawiono wyniki badań gleb wykonanych na terenie Raciborza-Markowic. Gleby Raciborza zostały zalane falą powodziową w roku 1997, co mogło spowodować zanieczyszczenie gleb metalami ciężkimi naniesionymi przez wody. Badania objęły oznaczenia zawartości makroskładników i mikroskładników gleb, wapnia, żelaza, manganu, siarki, biodostępnego magnezu, potasu i fosforu, a także zawartości metali ciężkich (ołowiu, kadmu, cynku, chromu, niklu i miedzi), przewodności elektrolitycznej, kwasowości gleby oraz zawartości materii organicznej. Analiza wykazała naturalną zawartość metali ciężkich, jednak badane gleby cechują się niedoborem makroskładników, takich jak fosfor, magnez i wapń.

#### Summary

The research of the soil quality was made in Markowice, the district of Racibórz, the town situated in the South of Poland. The soils of Racibórz were expected to be contaminated with heavy metals after the heavy flood in 1997, which devastated great part of Poland, especially the town. The assays covered macro- and microcomponents, contents of total calcium, iron, manganese, sulphur, bioavailable magnesium, potassium and phosphorus, contents of heavy metals (lead, cadmium, zinc, chromium, nickel and copper), electrolytic conductivity, pH of soil, and finally organic matter content in soil. The research showed that soils of the district of Racibórz have a natural content of heavy metals, but the soils have the deficiency of macrocomponents, such as phosphorus, magnesium and calcium.

#### INTRODUCTION

Research regarding environmental protection and engineering is carried out both in Poland and all over the world. Investigations into soil quality are part of it. There are numerous methods to examine the state of soil [1]. They cover contents and forms of macro and microelements or assay permissible contents of particular elements in different types of soil. Researchers also examine the impact of anthropogenic factors on the condition and quality of soil. Lots of laboratories focus on the effect of contaminants present in soil on living organisms. This wide range of research enables us to obtain a lot of valuable information.

Racibórz is a town situated in the south of Poland, near the Odra River in the region of Silesia. The district of Racibórz, Markowice, is situated north-east of the Ulga canal (Fig. 1). As far as soil types are concerned, Markowice can be divided into the area along the canal dominated by alluvial soil and histosols, and the eastern area dominated by podzol soils and cambisols.

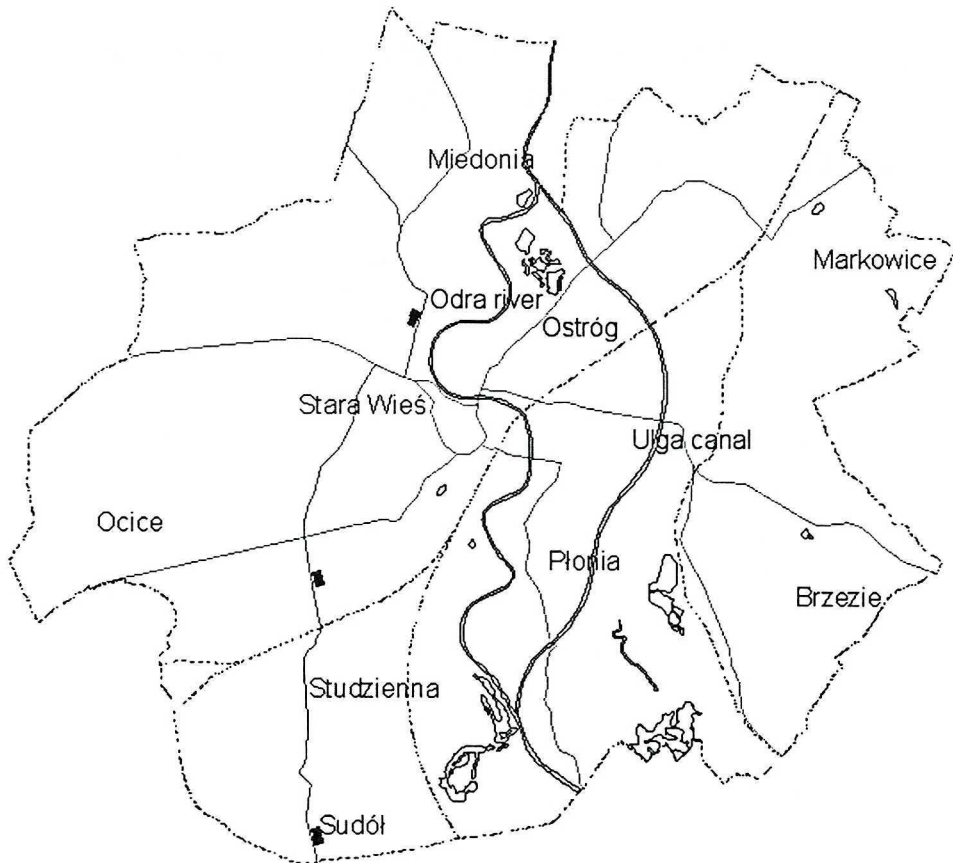


Fig. 1. Map of Racibórz commune (N = 50°06', E = 18°14')

The research was aimed at assaying macro- and microcomponents of soil to investigate the changes in soil quality after the heavy flood of 1997 which devastated most of the region. The analyses covered macro- and microelements contents of total calcium, iron, manganese, sulphur, plant available magnesium, potassium and phosphorus, contents of heavy metals (lead, cadmium, zinc, chromium, nickel and copper), electrolytic conductivity, pH of soil, and organic matter content in soil.

## EXPERIMENTAL

A sampling point was selected regularly using a geographical grid and map of Racibórz.

193 samples were collected from an area of 386 ha, each of them consisting of approximately 30–40 subsamples taken with an Egner's Soil Sampler. The samples were dried, homogenized and prepared for chemical analyses with reference to standards [4, 8, 12]. Samples 1–70 covered podzol soils and cambisols while samples 71–193 dealt with alluvial soil and histosols.

Each assay result was an average of 3 measurements. When the difference between the results exceeded 3 s (standard deviation), the tests were repeated and discrepancies were omitted. Each data set was analyzed statistically using Microsoft Excel 2000. Podzol soils with cambisols and organic histosols with alluvial soil were analyzed separately due to the soil types.

Total calcium in soil was assayed by digesting 150 mg of soil with a mixture of 2.5 cm<sup>3</sup> HNO<sub>3</sub> conc. and 0.6 cm<sup>3</sup> HF conc. (Suprapur Merck) in a microwave Milestone MEGA 1200. The resulting solution was diluted to 100 cm<sup>3</sup> with demineralized water. The assay was carried out using Schinkel buffer (Merck). The apparatus used was AAS, Varian, Spectr AA 880, using the flame technique. It was calibrated with 1 mg Ca/cm<sup>3</sup> standard solution (Merck).

Plant available magnesium was measured by the method presented in standard [9]. Its extraction from soil was carried out with CaCl<sub>2</sub> solution. Magnesium determination was carried out by FAAS, using an apparatus Varian, type Spectr AA 880 calibrated with 1 g Mg/dm<sup>3</sup> standard solution (Merck).

Plant available potassium was assayed by Egner – Riehm method [10], flame technique, using an apparatus AAS, Varian, type Spectr AA 880. Potassium was extracted from soil with calcium lactate and a suitable addition of HCl. The apparatus was calibrated with 0.1 mg K<sub>2</sub>O/cm<sup>3</sup> standard solution (Merck).

Iron and manganese were determined by FAAS using an apparatus Varian Spectr AA 880. The soil sample was digested identically to calcium. The apparatus was calibrated with standard solutions of 1 g Fe/dm<sup>3</sup> or 1 g Mn/dm<sup>3</sup> (Merck).

Heavy metals (lead, cadmium, nickel, chromium, copper and zinc) were assayed following the procedure in standard [6]. The sample was digested with concentrated HF and HNO<sub>3</sub>. Metal contents were determined by FAAS using an apparatus Varian Spectr AA 880. The apparatus was calibrated with 1 mg metal/dm<sup>3</sup> standard solutions for the metals mentioned above (Merck).

Plant available phosphorus was assayed by Egner – Riehm method through its extraction with calcium lactate and spectrophotometric method using ammonium molybdate [11].

Sulphur was determined by the method described in [3]. The sample was treated with Mg(NO<sub>3</sub>)<sub>2</sub> and heated at 550°C. Then it was transferred into HNO<sub>3</sub> solution, filtered, and sulfate ions were assayed turbidimetrically as BaSO<sub>4</sub> solution in the resulting filtrate. Calibration was carried out with dried, analytically pure K<sub>2</sub>SO<sub>4</sub>.

pH of soils was determined in 1 M KCl solution following the procedure presented in standard [5].

Soil electrolytic conductivity was determined according to the procedure illustrated in standard [7].

Organic matter was measured by determining organic carbon through wet oxidation by a dichromate – sulphuric acid mixture [3], and then the carbon contents were converted to organic matter content.



## RESULTS AND DISCUSSION

The lowest and highest contents of the elements, the values for soil pH and electrolytic conductivity are given in Table 1. The results are expressed in mg/kg of soil, electrolytic conductivity – mS/m, and  $P_2O_5$  – mg/100 g of soil.

Table 1. Lowest and highest contents of individual analytical assays in soils

Assay	Results					
	Lowest	Highest	Mean	Standard deviation	Mean (podzoluvis ols)	Mean (alluvial soil)
Ca	285	8632	2603.5	1725.6	1213.2	3394.7
Mg	30	1083	326.8	207.3	156.8	423.5
K	85	1191	348	152.7	265.1	395.2
Fe	4743	44073	21612.6	11573.1	11089.6	27601.4
Mn	43	1211	475.1	229.7	417.9	507.6
Pb	14.3	118.3	31	11.3	26.9	33.3
Zn	17.3	646.4	93.2	61.8	58.5	112.9
Cd	0	3.1	0.6	0.5	0.3	0.8
Cu	6.5	85.1	24.5	12.7	16.6	29.1
Ni	2.6	51.3	25.9	14.9	11.6	34
Cr	3.7	194.8	28	19.8	15.9	34.9
S	40	1724	238.2	211.2	132.5	298.3
$P_2O_5$	1.9	70.1	18.9	12.7	24.6	15.6
pH	3.4	7.4	4.9	0.9	4.8	5.1
Electrolytic conductivity	3	26	9.3	4	7.4	10.4

Fig. 2 shows the results of determination of calcium, plant available magnesium and potassium for Markowice; the highest and lowest values were omitted as negligible. The results for calcium are presented in Fig. 2a. The most of the results for podzol soils fell within the range of 0–1000 mg calcium/kg soil, the number of higher contents rapidly decreased. Probably, some calcium occurs in unavailable forms, which is confirmed by Fig. 6 illustrating the determinations of soil acidity. Over 100 of the soil samples in the data set revealed elevated acidity. As for the scatter of calcium results for alluvial soils, it represented a regular Gauss curve, and the maximum of samples was within 3000–4000 mg/kg soil.

Potassium content (Fig. 2b) represents irregular Gauss curves. In podzol soils, the maximum fell within 200–300 mg potassium/kg soil, whereas for alluvial soils and histosols, it ranged from 300–400 mg K/kg soil.

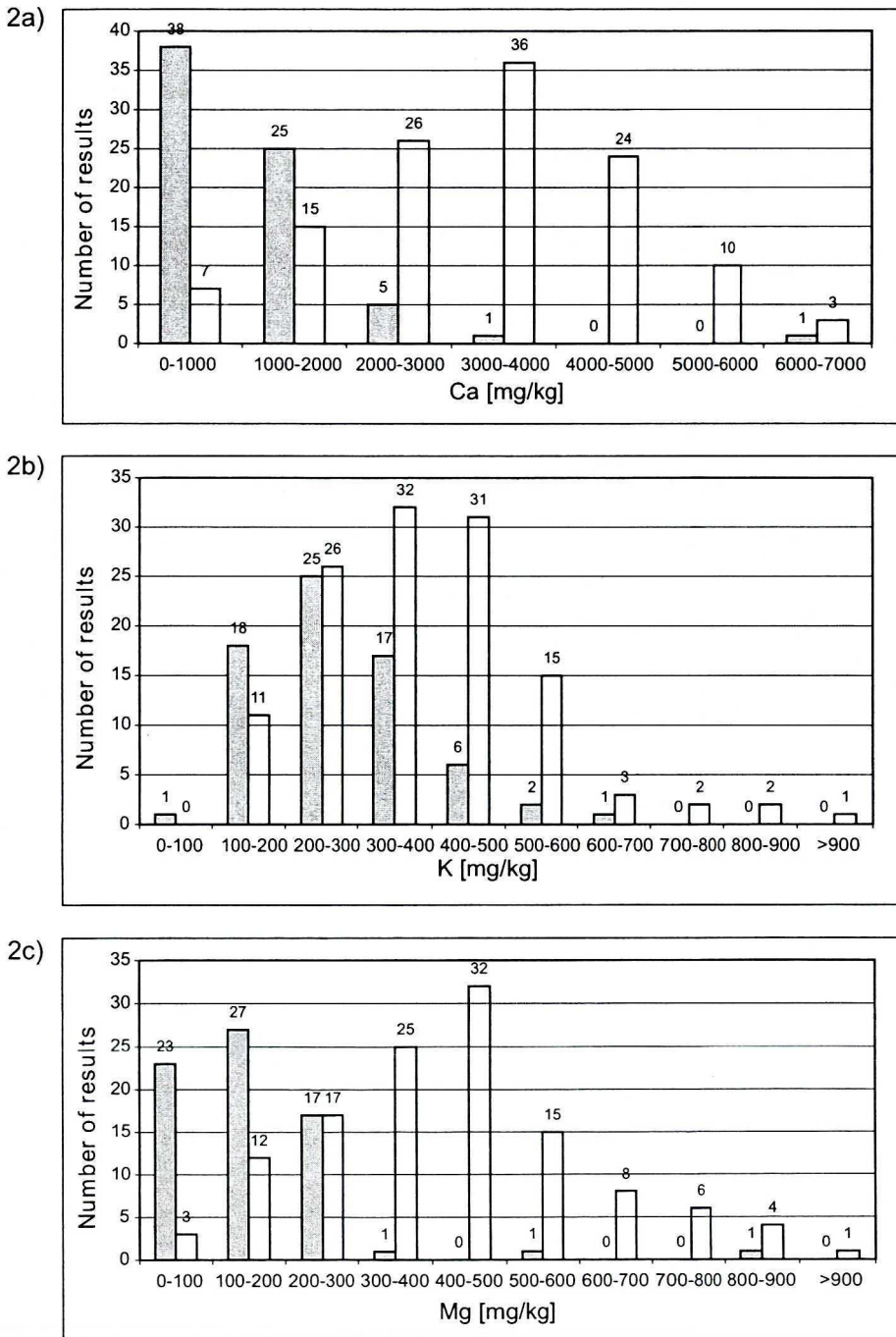


Fig. 2. The distribution of results for calcium (2a), potassium (2b) and plant available magnesium (2c) for soils of the Markowice region (the figures show amounts of results in dependence on contents of elements and soil types [mg/kg], the grey color means results for podzoluvisols and the white color means results for alluvial soils on the presented diagram)

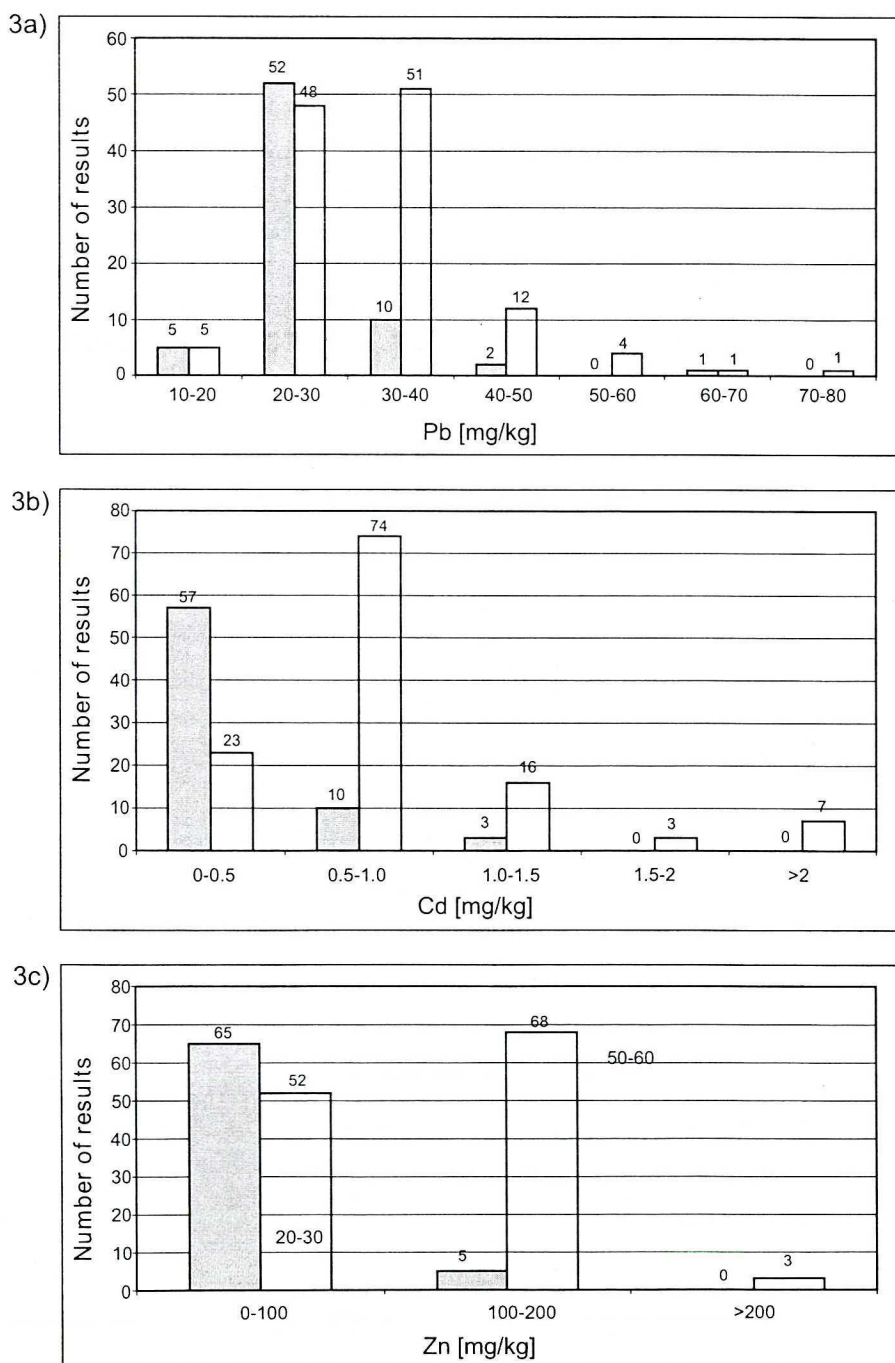


Fig. 3. The distribution of results for lead (3a), cadmium (3b) and zinc (3c) for soils of the Markowice region (the figures show amounts of results in dependence on contents of elements and soil types [mg/kg], the grey color means results for podzoluvisols and the white color means results for alluvial soils on the presented diagram)

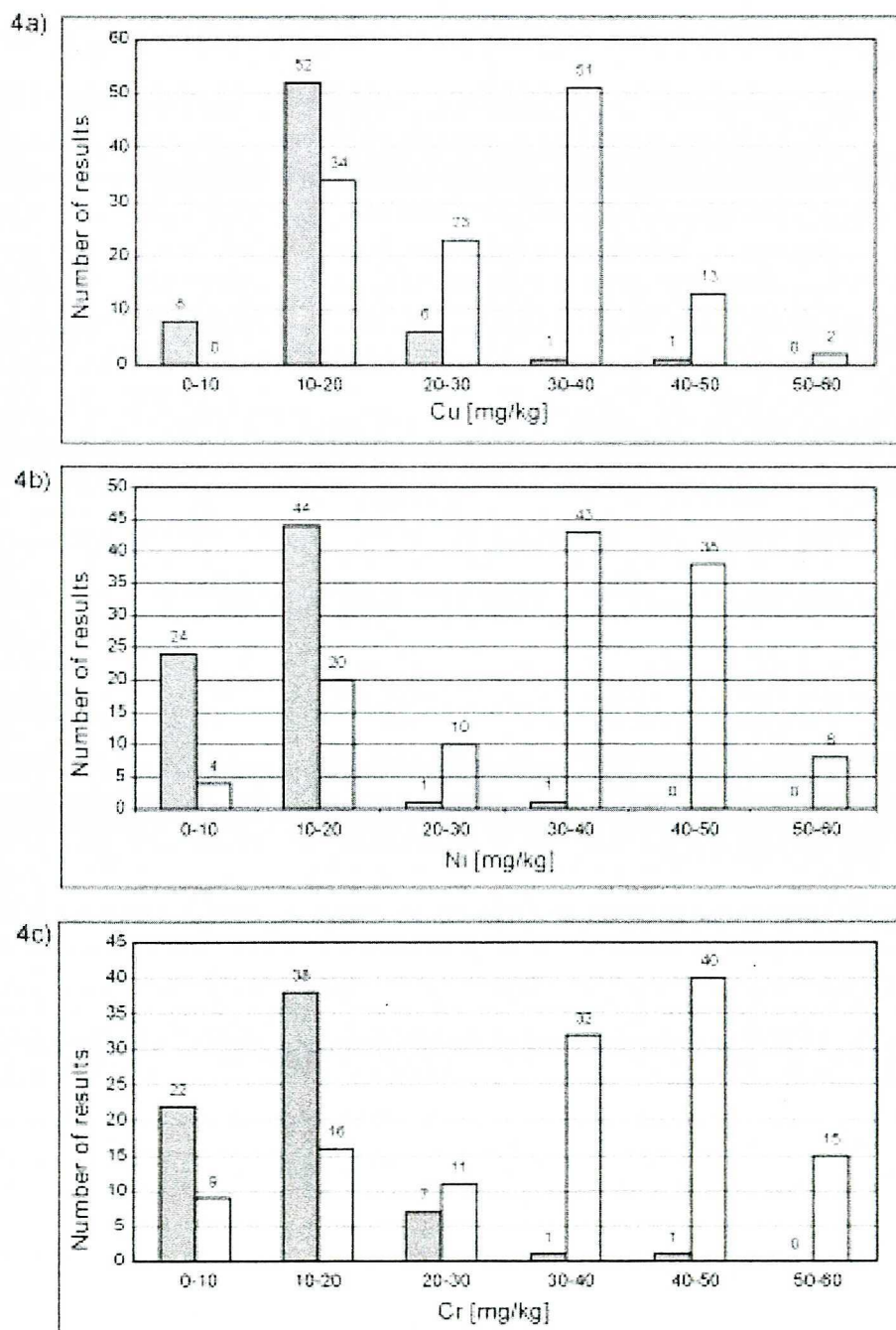


Fig. 4. The distribution of results for copper (4a), nickel (4b) and chromium (4c) for soils of the Markowice region (the figures show amounts of results in dependence on contents of elements and soil types [mg/kg], the grey color means results for podzoluvisols and the white color means results for alluvial soils on the presented diagram)

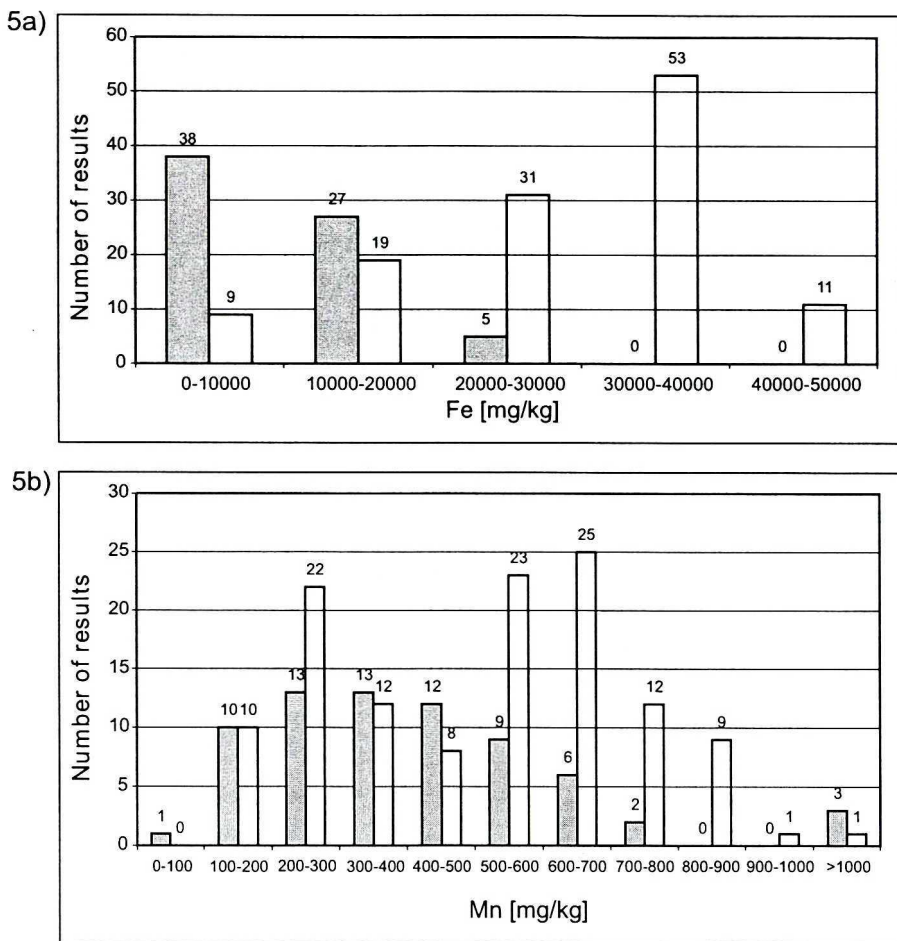


Fig. 5. The distribution of results for iron (5a) and manganese (5b) for soils of the Markowice region (the figures show amounts of results in dependence on contents of elements and soil types [mg/kg], the grey color means results for podzoluvisols and the white color means results for alluvial soils on the presented diagram)

The distribution of results for plant available magnesium (Fig. 2c) in podzol soils reached its maximum between 0 and 200 mg/kg soil. When the contents exceeded 300 mg/kg soil, the number of the results decreased. As for alluvial soils, the most of the results were found to be 300–500 mg Mg/kg soil.

Most of the results concerning heavy metals (Figs 3 and 4) demonstrated contents lower than permissible values. There are areas, however, where elevated zinc (3 samples: 355 mg/kg soil, 428 mg/kg soil, 646 mg/kg soil), lead (118 mg/kg soil) and cadmium (3.1 mg/kg soil) contents were found. This occurred mainly in the area along the Ulga canal. No documented causes for this problem are available. It is probably due to the illegal disposal of waste (batteries, paints etc.), or water carrying waste containing metals from other regions during the flood. The assays of heavy metals in podzol soils (Fig. 3) revealed that the largest quantity of results concerning lead contents fell within 20–30 mg/kg soil, cadmium



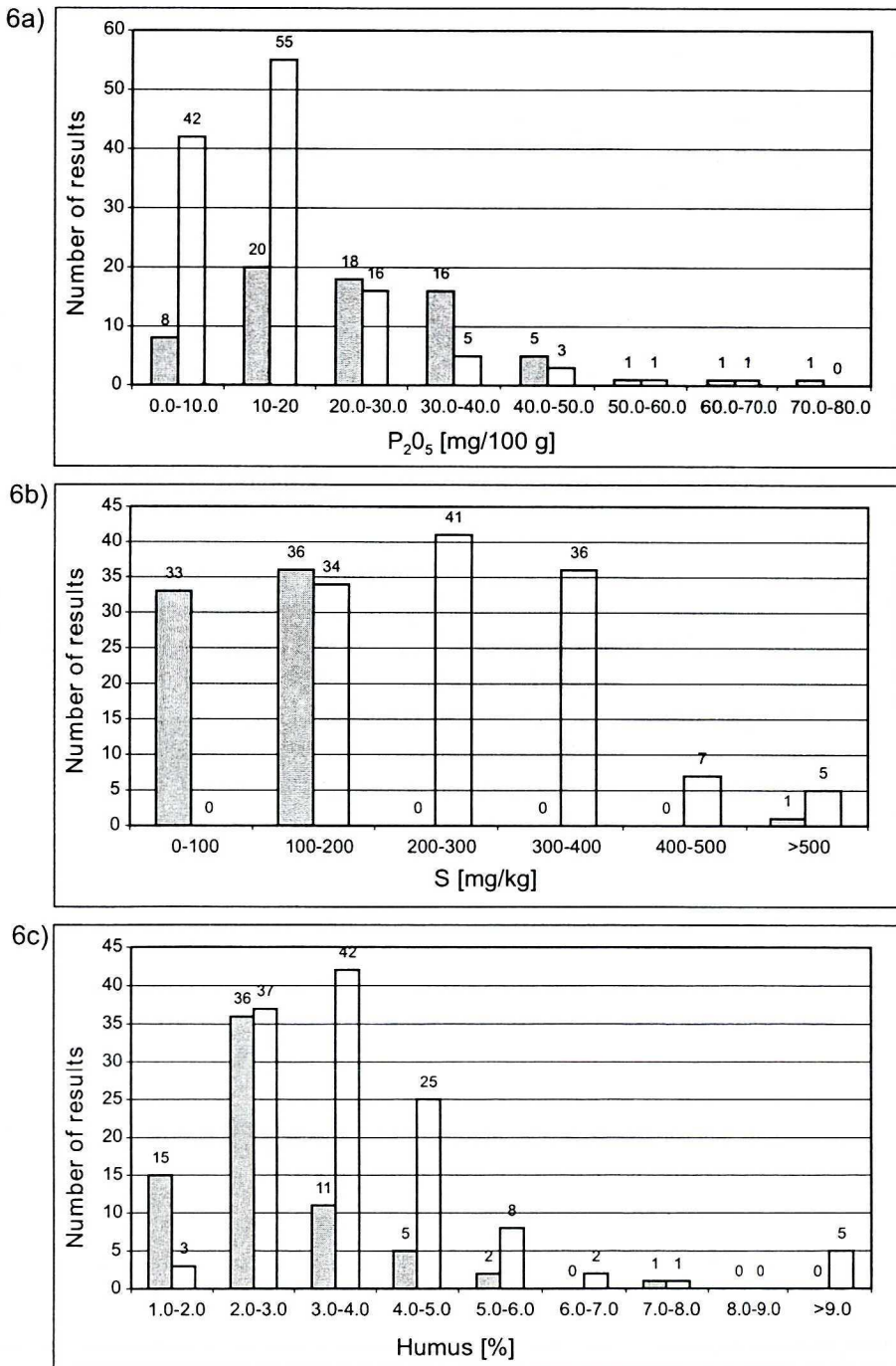


Fig. 6. The distribution of results for plant available phosphorus (6a) and total sulphur (6b) and humus (6c) for soils of the Markowice region (the figures show amounts of results in dependence on contents of elements and soil types [mg/kg], the grey color means results for podzoluvisols and the white color means results for alluvial soils on the presented diagram)

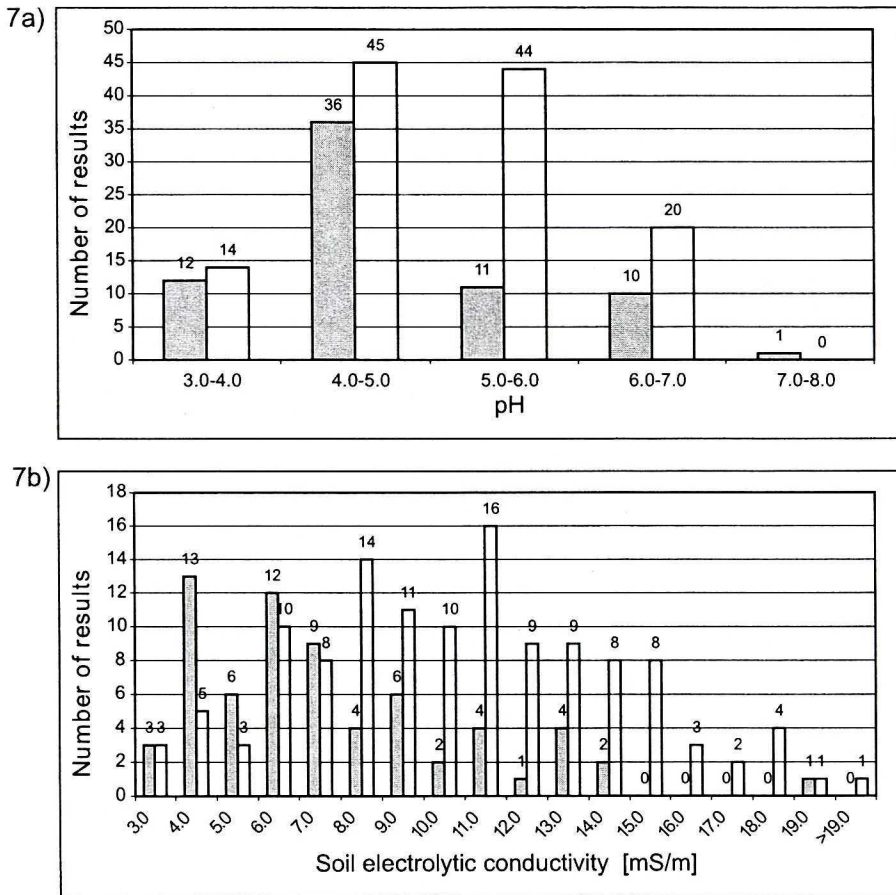


Fig. 7. The distribution of results for pH (7a) and electrolytic conductivity (7b) for soils of the Markowice region (the figures show amounts of results in dependence on contents of elements and soil types [mg/kg], the grey color means results for podzoluvisols and the white color means results for alluvial soils on the presented diagram)

between 0 and 0.5 mg/kg soil, zinc 0–100 mg/kg soil, copper, nickel and chromium between 10 and 20 mg/kg soil. As for alluvial soils, the largest amount of results on lead contents were found between 20 and 40 mg/kg, cadmium 0.5–1 mg/kg soil, zinc 0–200 mg/kg soil, copper 10–40 mg/kg, nickel 20–50 mg/kg soil and chromium 10–50 mg/kg soil.

In podzol soils, iron displayed the most numerous results (Fig. 5a) within 0–10000 mg/kg soil, which decreased at 30000 mg/kg soil. As far as the alluvial soils are concerned, iron contents increased and reached their maximum between 30000 and 40000 mg/kg soil. The number of samples at higher iron contents was negligible.

As for manganese contents in podzol soils, the maximum of samples fell within 200–400 mg/kg soil (Fig. 5b). The number decreased at 800 mg/kg. In alluvial soils, there were two maximums: 200–300 and 500–700 mg/kg soil. Generally, manganese contents in samples oscillated between 100 and 900 mg Mn/kg. It seems that they are too low for the proper growth of plants.

Plant available phosphorus ( $P_2O_5$ ) contents (Fig. 6) in podzol soils show similarities as far as the values of the amount of samples in the range of 10–40 mg  $P_2O_5$ /100 g soil are concerned, while in the alluvial soils the most numerous results fell within 2–20 mg/100 g soil.

The largest amounts of results for sulfur contents in podzol soils were observed in the range of 40–200 mg S/kg soil, while for the alluvial soils, it was 100–4000 mg S/kg soil.

Organic matter content in podzol soils reached its maximum between 2 and 3%, while for the alluvial soils it was 2–5%. The samples of 1–5% content were most numerous. Organic matter content in soil increases buffering capacity and sorption of hydrogen ions.

The most frequent pH values in podzol soils and alluvial soils were 4–5 and 4–6 respectively. Fig. 7 shows statistical scatters of pH and electrolytic conductivity determinations in the soil. The lowest and highest pH values were 3.35 and 7.4 respectively. Approximately 13% of the soil samples had pH of 3–4, and the largest amounts of results fell within the range of 4–5.

Electrolytic conductivity of soil was found to be 3–19 mS/m, the maximums for podzol soils and alluvial soils being 4 mS/m and 12 mS/m respectively.

The largest number of results for electrolytic conductivity in podzol soils fell within 4–7 mS/m, while for the alluvial soils; it was 8–11 mS/m.

## CONCLUSIONS

The soil in Racibórz-Markowice after the flood of 1997 does not show any considerable changes in the quality of farmland according to the data presented by Kościelniak et al. [2].

Calcium content in podzol soils is lower by at least 50% compared to alluvial soils. It seems to be sufficient in respect of plant demand; however, its chemical form does not reduce soil acidity. Under the conditions of strong soil acidity, a higher contribution of calcium and magnesium is required.

Potassium content in researched soils is sufficient for plants, although it is lower by 1/3 in podzol soils than in alluvial soils.

Magnesium content is also sufficient, although it is 2–3 times lower than in alluvial soils.

Most of soils do not exceed the permissible contents of heavy metals. Our investigation shows that elevated contents of zinc, lead and cadmium were found in 5 samples along the Ulga canal. These areas can be used for industrial plant cultivation and the soil should be reclaimed by applying e.g. biological methods.

Iron content in podzol soils is 10 times lower than in alluvial soils.

Podzol soils were characterized by higher phosphorus contents compared to alluvial soils.

Sulfur content in alluvial soils is twice as low as in podzol soils.

Podzol soils, due to their weak sorption complex, reveal higher acidity, whereas some results for alluvial soils are closer to neutral values.

Electrolytic conductivity in podzol soils is twice as low as in alluvial soils.

## REFERENCES

- [1] Cameron R.E.: *Guide to site and soil description for hazardous waste site characterization*, EPA, March 1992.

- [2] Kościelniak W., L. Szerszeń, H. Terelak, J. Kaszubkiewicz, A. Karczewska, M. Roschke: *Wpływ powodzi lipcowej w 1997 roku na właściwości gleb doliny Odry i Nysy Kłodzkiej oraz ich zanieczyszczenie metalami ciężkimi*, Pamiętnik Puławski, 115, 5–15 (1999).
- [3] Ostrowska A., S. Gawliński, Z. Szczubiałka: *Methods for analysis and evaluation of soil and plant characteristics*, (in Polish) 1<sup>st</sup> ed., Instytut Ochrony Środowiska, Warsaw 1991.
- [4] PN-ISO 10381-6 *Quality of soil. Sample collection. Rules on the collection, treatment and storage of samples intended for investigating aerobic microbiological processes under laboratory conditions* (in Polish).
- [5] PN-ISO 10390 *Soil quality. pH determination* (in Polish).
- [6] PN-ISO 11047 *Soil quality. Determination of cadmium, chromium, cobalt, copper, lead, manganese, nickel and zinc soil extracts by aqua regia. Methods of flame and electrothermal atomic absorption spectrometry* (in Polish).
- [7] PN-ISO 11265 *Soil quality. Determination of electrolytic conductivity* (in Polish).
- [8] PN-ISO 11464 *Quality of soil. Preliminary sample preparation for physicochemical analysis* (in Polish).
- [9] PN-R-04020 *Chemical and agricultural soil analysis. Determination of bioavailable magnesium* (in Polish).
- [10] PN-R-04022 *Chemical and agricultural soil analysis. Determination of bioavailable potassium in mineral soils* (in Polish).
- [11] PN-R-04023 *Chemical and agricultural soil analysis. Determination of bioavailable phosphorus in mineral soils* (in Polish).
- [12] PN-R-04032, PN-R-04033 *Soils and mineral deposits. Division into fractions and granulometric groups* (in Polish).

Received: December 28, 2005; accepted: April 20, 2006.